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MECHANICAL BEHAVIOR OF POLYCRYSTALLINE
NON-METALLICS AT ELEVATED TEMPERATURE

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MECHANICAL BEHAVIOR OF POLYCRYSTALLINE NON-METALLICS
AT ELEVATED TEMPERATURE
(SC-NGR-05-020-084)

I. Equipment for Creep Testing

During the last six months, two dead load compression creep units have been modified to extend the range of stresses and creep rates over which they can operate and to make their operation easier and more accurate. One of these units was the one used for the NaCl creep tests reported in the last progress report. Both units have atmosphere control capabilities.

The modifications included moving the load pan from the top of the unit to the bottom, as shown in Figure 1. The load is applied to the sample by means of a self-balancing framework. Heavier loads can now be used because no bending forces are introduced to load ram, as was the case when weights were placed on top of the load pan above the sample.

Sample deflection can be measured accurately with a single dial gage mounted colinear to the sample. This was not possible when the load pan was above the sample. Two dial gages were required to measure the load pan deflection and to average the bending of the pan.

An LVDT has been added for recording sample deformation during slow or rapid tests.

The equipment for testing Al_2O_3 is nearly complete. It is hoped that all phases of equipment construction will be finished in the next two months, and full time testing of Al_2O_3 and NaCl can begin.

II. Equipment for Density Measurements

An analytical balance was secured on loan from the Center for Materials Research and set up for density measurements utilizing Archimedes principal.

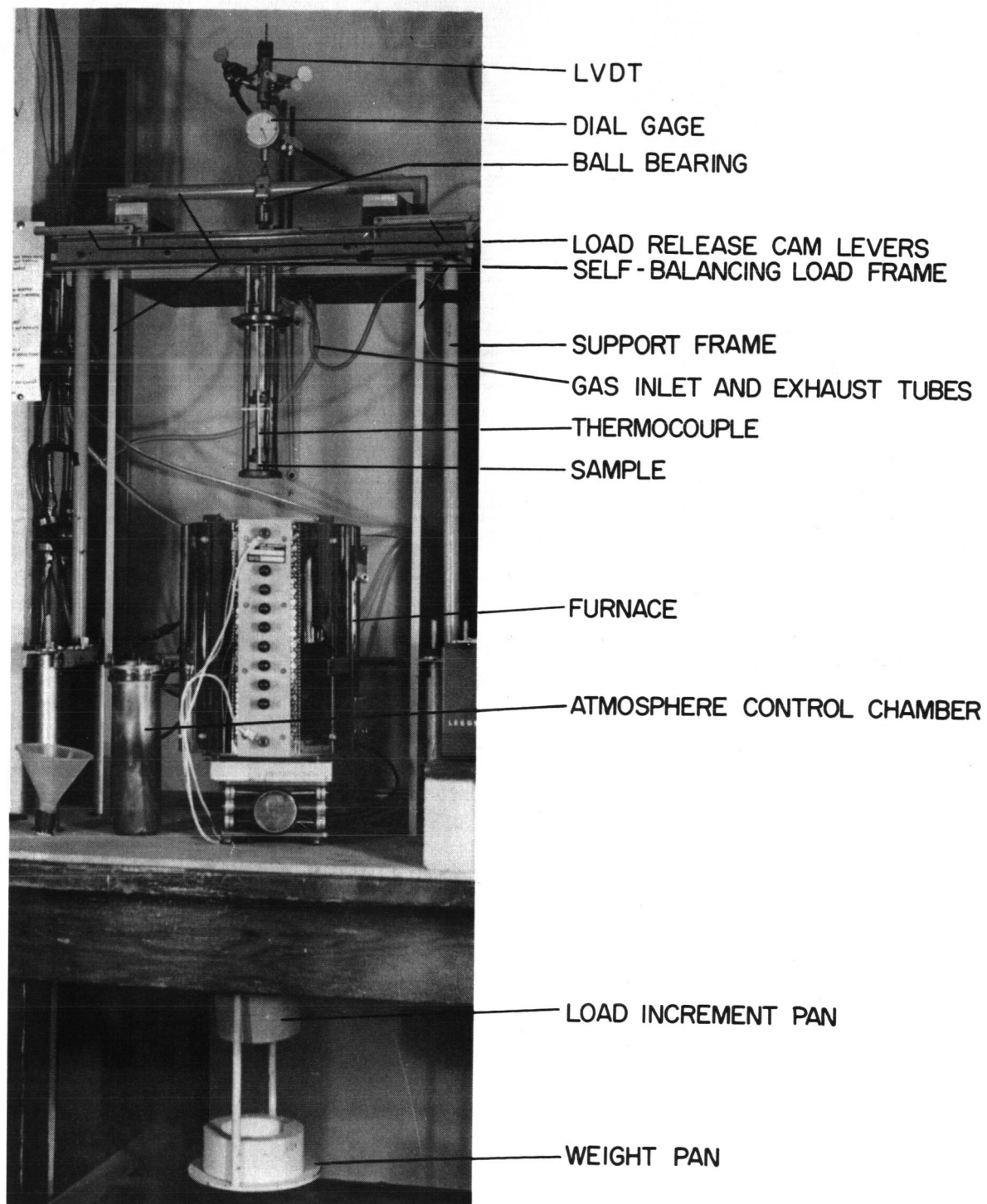


Fig. 1 Compression creep unit

It will be used to determine density changes occurring during deformation, particularly those resulting from void formation and grain boundary separation.

III. Diffusion in Sodium Chloride (P. Burke, Doctoral candidate)

The creep rate controlling mechanism for metals involves the climb of dislocations over barriers^(1, 2) or else the non-conservative motion of jogs or kinks on screw dislocations.^(1, 3) Both of these mechanisms involve diffusion of vacancies to or away from dislocations and a stress exponent of about $n = 5$. Since n for creep in sodium chloride has been found to be 5 (Section V of this report), it is assumed that the same mechanisms are operating in both pure metals and sodium chloride.

In sodium chloride two kinds of ions diffuse, one kind more rapidly than the other. Since the climb of dislocations or the motion of jogs on dislocations requires the diffusion of both kinds of ions in order to maintain stoichiometry and to preserve the crystal lattice, the slower diffusing species will be creep rate controlling. The activation energy for creep will be approximately equal to the activation energy for self diffusion of the slower moving species.

Chlorine usually diffuses more slowly than sodium, although the presence of grain boundaries, dislocations and divalent anion impurities may enhance chlorine diffusion and retard sodium diffusion so that sodium becomes the slower moving species.

Experimental results of several investigators⁽⁴⁻¹⁰⁾ showing the temperature dependence of sodium and chlorine diffusion are plotted in Figure 2. A theoretical study of diffusion in sodium chloride, especially as influenced by grain boundaries, has been started and will be discussed in

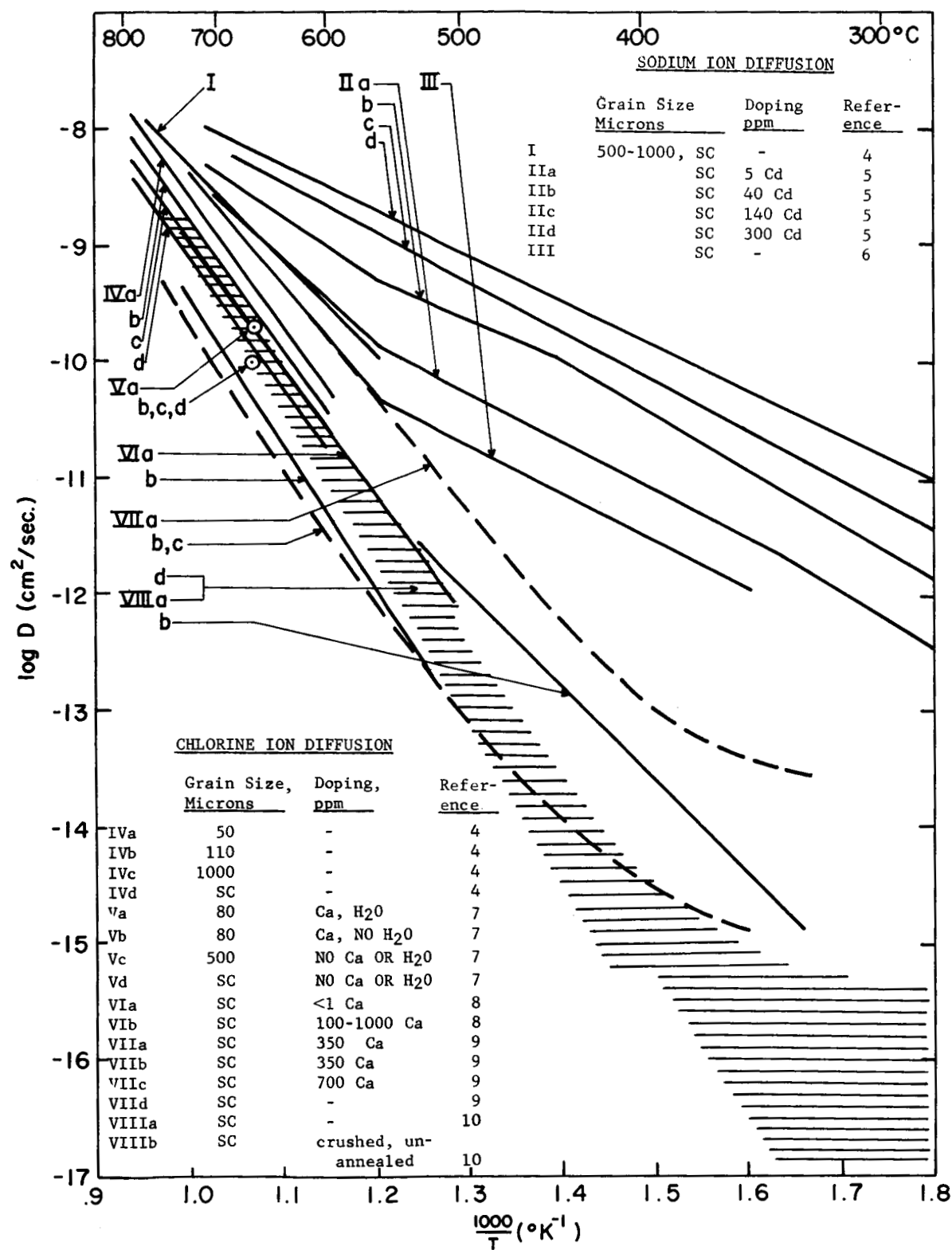


Fig. 2 Diffusion coefficients of sodium and chlorine in sodium chloride versus reciprocal absolute temperature.

the next progress report. Such studies should be helpful towards understanding the mechanical behavior of ionic polycrystals at elevated temperatures.

IV. Young's Modulus of Sodium Chloride (Y. Miyazawa, Graduate Research Assistant)

Very little is yet known about the influence of temperature on the elastic properties of polycrystalline sodium chloride. It is known⁽¹¹⁾ that the creep rate of pure polycrystalline metals is a function of the elastic modulus as well as stress, diffusion coefficient and other factors. In our study of creep of polycrystalline sodium chloride, it is necessary to know Young's Modulus at creep test temperatures in order to calculate meaningful activation energies. For this reason, an experimental study of the modulus of polycrystalline sodium chloride was initiated.

Experimental Techniques

Sodium chloride samples of two different grain sizes were prepared to measure dynamic Young's Modulus. The first samples were made by extruding single crystals; a second kind of sample was made by compacting sodium chloride powder containing .06 weight percent aluminum oxide particles (0.1 micron). The aluminum oxide particles were added to stabilize the sodium chloride grain size. All samples made were typically 1/8" in diameter and 5" long. All samples were annealed at 700°C. The dynamic modulus was measured by inducing a both-end-free transverse vibration on the samples. Elevated temperature tests were performed by heating the specimens in an elliptical furnace. The heating source was a quartz lamp held at one focal point of the furnace. The specimen was supported at the other focal point by two pairs of chromel-alumel thermocouples at the two

nodal points of the specimen. Mechanical vibrations were induced into the specimen through a thin steel wire by means of an earphone. The response of the specimen to mechanical vibrations was detected through another steel wire to a Rochelle salt phonograph pick-up. Resonant frequencies of the samples were about 800C/S at room temperature.

Results

The influence of temperature and grain size on the dynamic Young's Modulus of polycrystalline sodium chloride is given in Figure 3. In the fine grain size sample, the Young's Modulus is seen to drop fairly rapidly at temperatures from 250°C to 650°C. This is very likely caused by grain boundary relaxation of the type commonly obtained in metallic systems. For the coarse grain size sample, grain boundary relaxation is not clearly observed. The results obtained are fairly consistent with values calculated from single crystal elastic constants using the Voight and Reuss method and data from L. Hunter and S. Siegel⁽¹²⁾ and F. C. Rose⁽¹³⁾. Also the results are in very good agreement with the data of S. V. Subrahmanyam⁽¹⁴⁾ in the temperature range from 30°C to 300°C. The latter author's samples were made by compacting <200 mesh (~74 micron) powdered NaCl.

V. Creep of Sodium Chloride (P. Burke, Doctoral Candidate)

Creep data for tests run to date are shown in Table I. This table includes data shown in the last progress report plus the results of tests conducted since then. Not included are data from tests in which the creep rate was so fast that it was not possible to adjust the load to maintain constant stress during the test.

Activation energies for diffusion can be determined from creep test data⁽¹⁵⁾ by plotting $\log \dot{\epsilon}$ versus $\log \sigma/E$, Figure 4, and $\log \dot{\epsilon}$ at constant

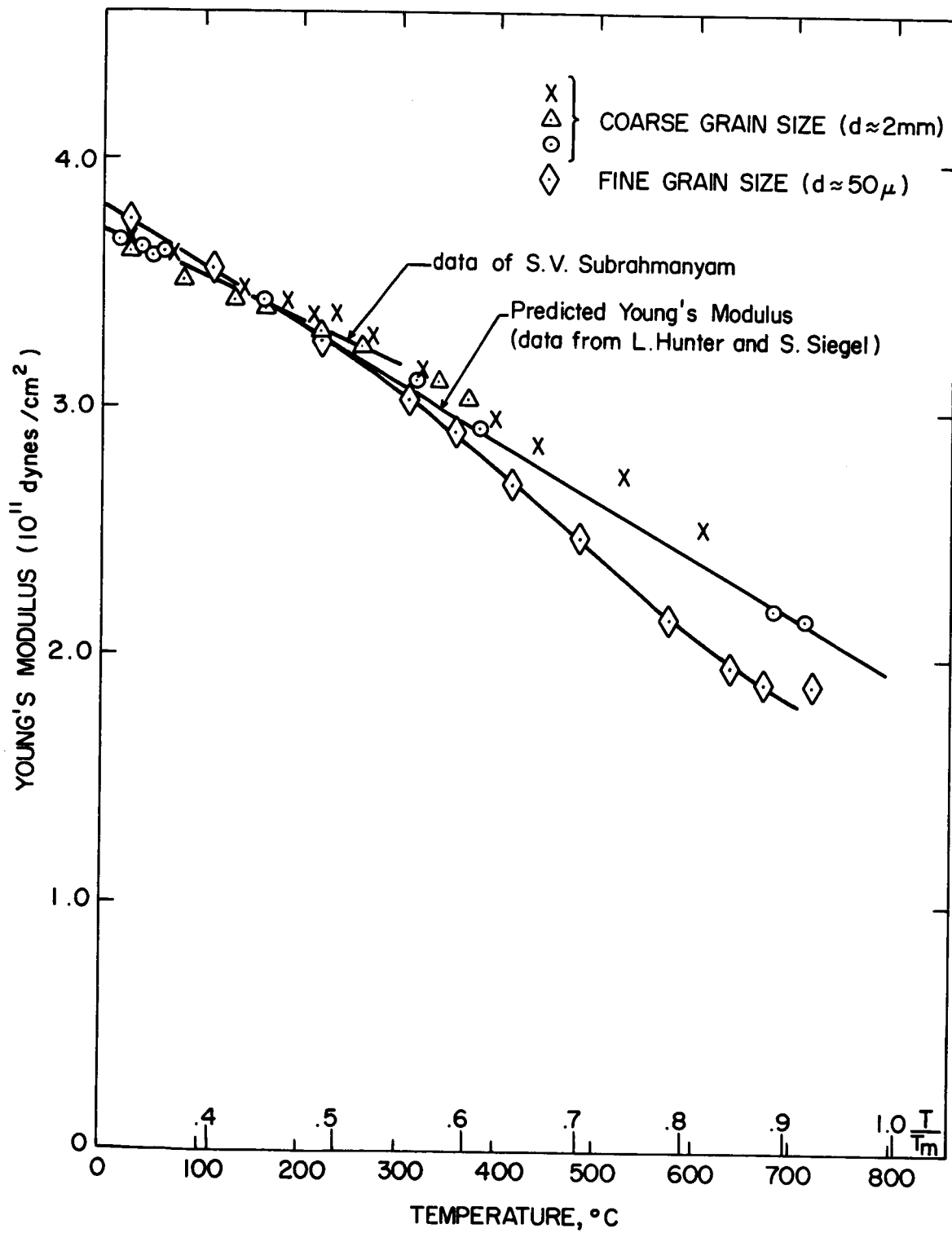


Fig. 3 Dynamic Young's modulus of polycrystalline sodium chloride.

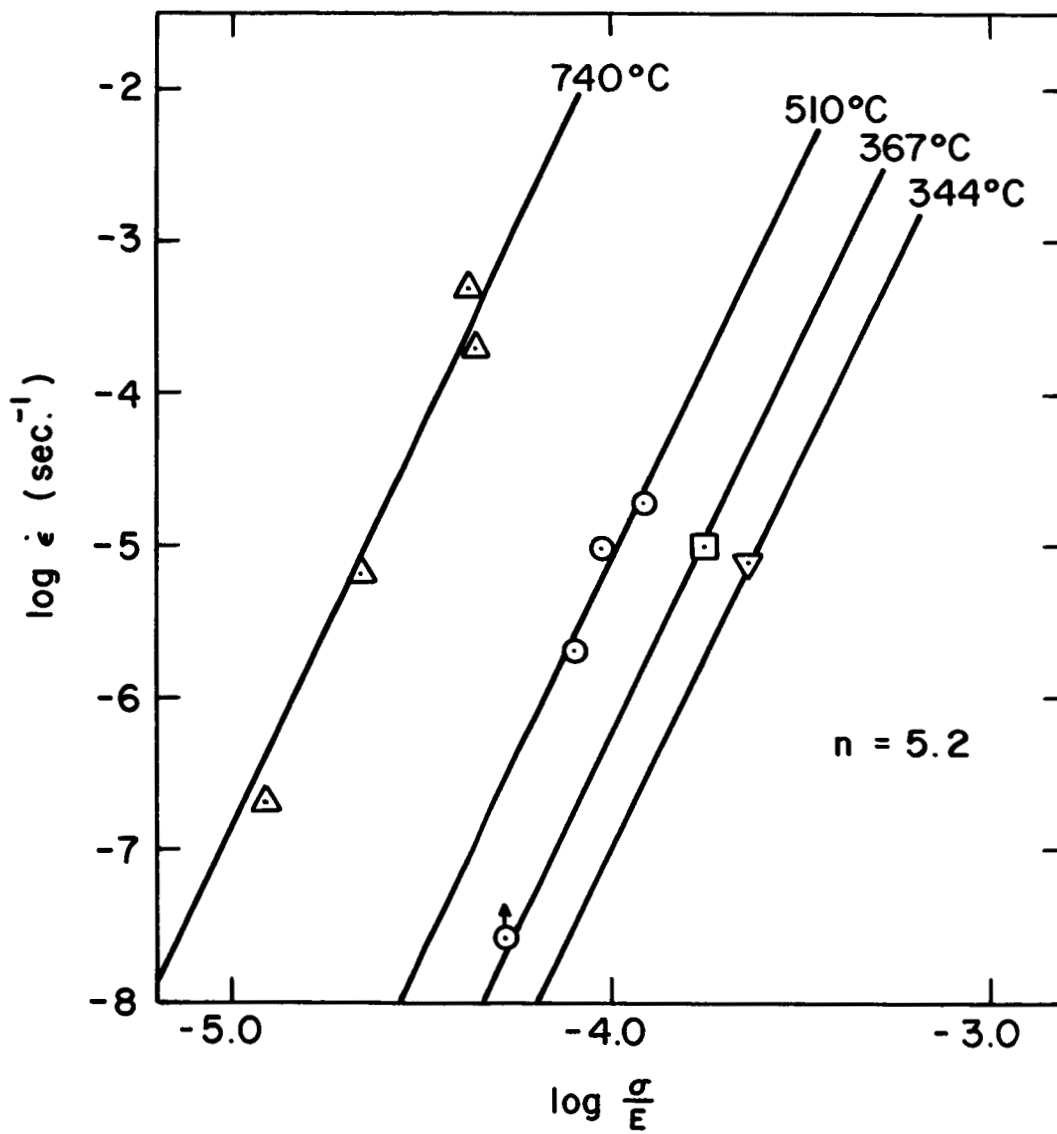


Fig. 4 Log steady state creep rate versus log creep stress - elastic modulus ratio for polycrystalline sodium chloride.

σ/E versus $1/T$, Figure 5, where $\dot{\epsilon}$ equals the steady state creep rate; σ , the creep stress; E , Young's modulus of elasticity, and T the absolute temperature. This is equivalent to determining the activation energy for creep from a plot of logarithm $\dot{\epsilon}$ at constant σ versus $1/T$ and then finding the activation energy for diffusion by subtracting a correction factor related to the change in E with T , as was done in the last progress report.

The activation energy for diffusion calculated from creep data in the temperature range 510° to 740°C is 55 kcal/mol. This agrees well with the results from chlorine diffusion studies in nominally pure as well as calcium doped sodium chloride. The experimentally determined activation energy for chlorine ion diffusion in this temperature range is 48 to 62 kcal/mol^(4, 8, 9, 10), that for sodium ion diffusion is 17 to 37 kcal/mol, depending on composition,^(4, 5, 6)

At lower creep temperatures the calculated activation energy for diffusion apparently drops to 22 kcal/mol. A large degree of uncertainty exists about these results because of the small amount of experimental data available. Future creep testing will be directed toward a more precise determination of activation energy as a function of temperature.

Strong evidence that the creep of sodium chloride is empirically similar to creep in pure metals and is proportional to the diffusion rate of chlorine may be obtained by plotting $\log (\dot{\epsilon}/D)$ versus $\log (\sigma/E)$, Figure 6, in accordance with the empirical relation for pure metals,

$$\dot{\epsilon} = AD\left(\frac{\sigma}{E}\right)^n.$$

A good correlation is obtained by using values of D for chlorine diffusion. This is not so if values of D for sodium diffusion are used. The points

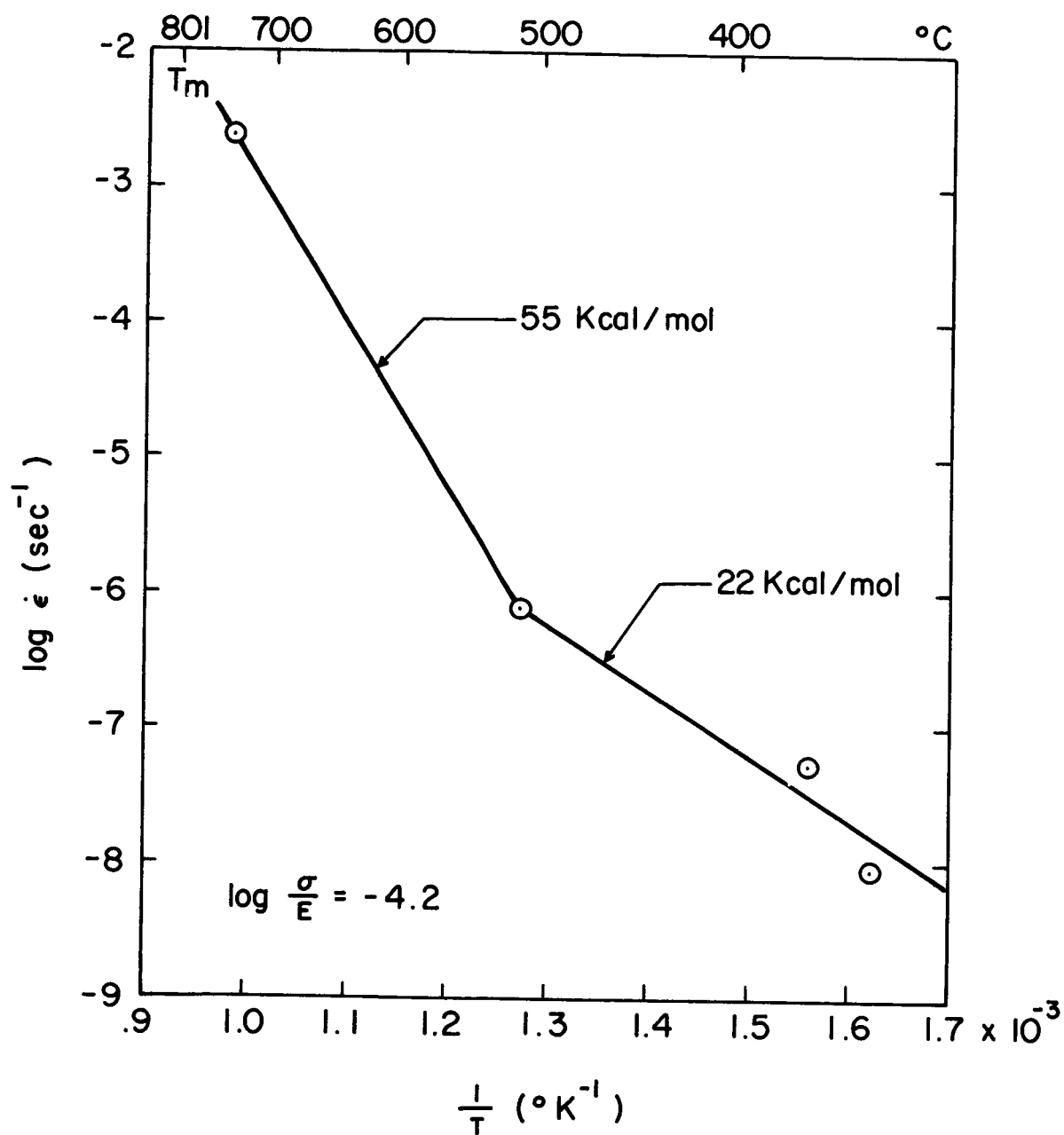


Fig. 5 Log steady state creep rate at constant stress-modulus ratio versus reciprocal absolute temperature for polycrystalline sodium chloride.

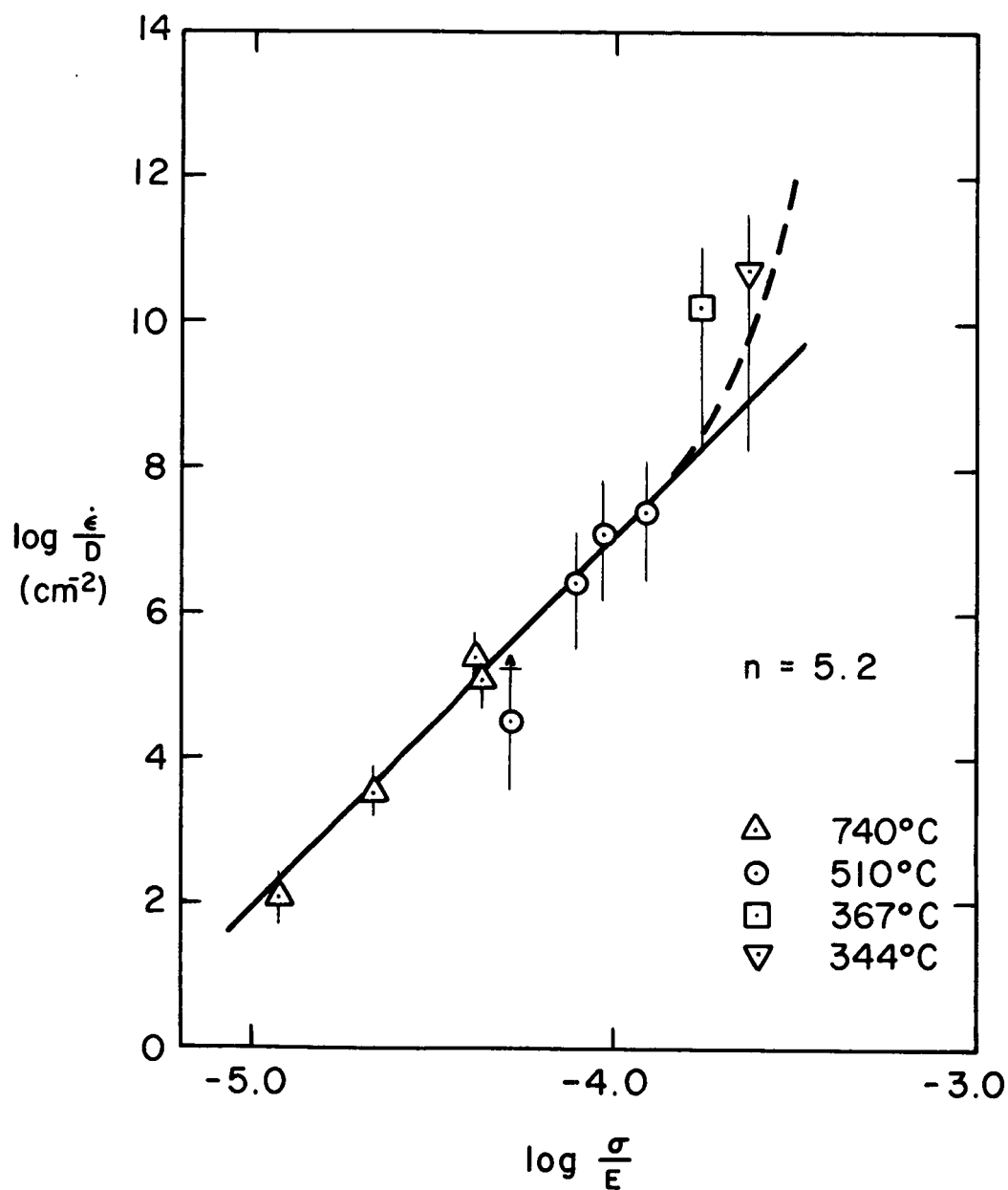


Fig. 6 Log steady state creep rate/chlorine diffusion coefficient ratio versus log stress/modulus ratio for polycrystalline sodium chloride.

plotted in Figure 6 represent the steady state creep rate divided by D_{G1} for polycrystalline sodium chloride as measured by Laurent and Bernard⁽⁴⁾ or extrapolated from their work. The vertical line through each point represents $\dot{\epsilon}$ divided by the maximum experimental range in D_{G1} values determined from all references shown in Figure 6.

Values for E were taken from the work of Miyazawa reported in this progress report.

The value of n obtained from Figure 6 is 5.2. This is quite consistent with n values for pure metals.

At high values of $\dot{\epsilon}/D$ there is a possible upswing in the curve.⁽¹¹⁾ This impression is strengthened by the fact that several new samples tested at low temperatures and high stresses deformed more rapidly than was expected by extrapolation of data in the linear power law region. Many metals exhibit an upswing in the $\log \dot{\epsilon}/D$ versus $\log \sigma/E$ curve at $\dot{\epsilon}/D \approx 10^9 \text{ sec}^{-1}$; and this trend seems to be obeyed also for polycrystalline sodium chloride.

VI. Creep of Sodium Chloride-Potassium Chloride (R. Cannon, Graduate Research Assistant)

The high temperature creep characteristics of certain metallic solid solutions are found to be different from those of pure metals.^(16, 17) The creep rate of these alloys is proportional to the stress to the third power instead of stress to the fifth power as is the case with pure metals. Other solid solutions, however, show the same stress dependence as pure metals.⁽¹⁸⁾

No one yet, to the author's knowledge, has determined the stress-creep rate characteristics of non-metallic solid solutions. Since creep

of polycrystalline sodium chloride is presently being studied under this contract, it was decided to initiate a study on the creep behavior of a sodium chloride-potassium chloride solid solution. The phase diagram for this system has a two phase immiscibility gap which extends up to 470°C ($0.71 T_m$). The liquidus region extends down to 675°C . Therefore, samples in solid solution of all compositions across the phase diagram may be tested in the temperature range 470 to 675°C . It is proposed to test several compositions including pure potassium chloride.

Thus far, time has been spent in learning how to fabricate the samples. Extrusion was thought to be a good way to produce fine grained polycrystalline samples. It was first thought that powder compaction and sintering might produce a good billet for extruding, but these billets were not homogeneous. It is possible to obtain homogeneous billets, however, by casting the powder in carbon dies in a helium atmosphere furnace.

Due to the greater strength of the solid solutions samples, they were more difficult to extrude than the pure sodium chloride samples. The extrusions usually exhibited an uneven surface. A new extrusion die is now being made which will withstand higher temperatures and which uses indirect extrusion. It is hoped that satisfactory extrusions can be made with this die.

Creep tests were performed on small lengths of extrusions which exhibited smooth surfaces. These tests showed that alloys of 50% sodium chloride - 50% potassium chloride have about twice the strength of pure sodium chloride at 510°C when compared at the same creep rate.

VII. Mechanical Behavior of Solids at Elevated Temperature (O. D. Sherby and P. M. Burke)

A report has been under preparation describing the various factors

influencing the mechanical properties of crystalline solids at elevated temperature. In this report we have attempted to compare the behavior of typical metallic materials with ionically and covalently bonded materials. A second draft of this report has been completed and it is anticipated that the final draft will become available by the end of this year.

In the report we approach the subject of mechanical behavior of materials at elevated temperature by examining the influence of the two main external variables, temperature and stress, on the creep strength. In addition, the structural variables that are important in creep are emphasized and such factors as grain size, elastic modulus and stacking fault energy, are discussed in detail. The phenomenological aspects of solid solution alloying on the strength of metals above one-half the melting temperature are evolving rapidly and these aspects are reviewed. It is well established that materials can be strengthened at high temperatures by addition of a hard second phase and this subject is also covered. The mechanisms of dispersion hardening, however, are not well understood at the present time and much additional fundamental work is needed here.

TABLE I
Steady State Creep Rate
As a Function of Stress and Temperature

<u>Test No.</u>	<u>Sample No.</u>	<u>Temp. T (°C)</u>	<u>Stress, σ (psi)</u>	<u>Creep Rate, $\dot{\epsilon}$ (sec⁻¹)</u>
4	2.1.2	512	365 305	8.1×10^{-6} 2.2×10^{-6}
7	2.1.1	512	470 200	1.8×10^{-5} $>2.8 \times 10^{-8}$
10	2.1.3	740	140 70	1.9×10^{-4} 7.0×10^{-6}
11	2.1.7	740	38.5 133	2.2×10^{-7} 4.8×10^{-4}
13	2.4.1	343	1050	8.6×10^{-6}
14	2.3.3	367	738	1.1×10^{-5}

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